AD-A174 472 METHODS FOR THE SYNTHESES OF MONO- DI- TRI- AND TETRANITRO DERIVATIVES OF DIPHENYLAMINE(U) WEAPONS SYSTEMS RESEARCH LAB ADELAIDE (AUSTRALIA) N J CURTIS 1/1

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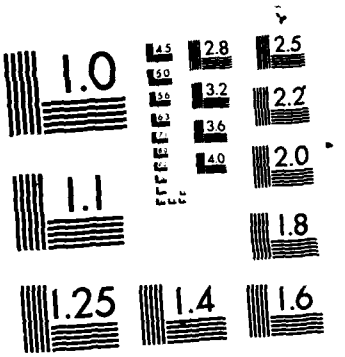

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TECHNICAL REPORT

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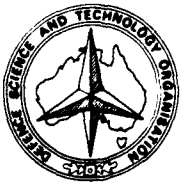
N.J. Curtis

S U M M A R Y

A critical review of the methods available for the syntheses of the title compounds is presented. Concise procedures are given for the preparation of these compounds, obtained in useful yield from readily available starting materials.



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1. INTRODUCTION

Diphenylamine, 2-nitrodiphenylamine and Akardite (1,1-diphenylurea) are commonly used stabilisers for propellants. Their action is to remove oxides of nitrogen formed in propellant decomposition by which they are converted to a range of diarylnitrosamines and nitrodiphenylamines. Nitration of the aromatic nuclei proceeds to an increasing extent with aging of propellant ultimately giving 2,2',4,4',6,6'-hexanitrodiphenylamine on extended storage at elevated temperatures (ref.1).

In accord with the *ortho/para* directing nature of the amine group and the deactivating influence of the nitro function, only those nitro derivatives of diphenylamine showing substitution in the 2-(6-) and 4- positions are found in propellants(ref.1,2), in appreciable amounts. A possible exception is 3-nitrodiphenylamine which has been reported found in propellants(ref.2) but its daughter products (2,3'-; 3,4'- and 3,5- isomers etc) have not been detected.

This report details and evaluates the methods that have been used to prepare those mono-, di-, tri- and tetranitrodiphenylamines which are potentially to be found in propellants. These preparations are generally dispersed throughout the chemical literature and are frequently described without reference to final yield. In a later section, experimental details are given by which this author has prepared samples of each of these compounds.

2. GENERAL SYNTHETIC METHODS

It should be noted that present "Chemical Abstracts" usage dictates that the diphenylamines should be named as a derivative of benzenamine. Thus diphenylamine is classed as a trivial name and is abstracted under benzenamine-,N-phenyl. Similarly, 2,4'-dinitrodiphenylamine is described as benzenamine,2-nitro-N-(4-nitrophenyl) and 2,4,4'-trinitrodiphenylamine is found under benzenamine, 2,4-dinitro-N-(4-nitrophenyl). To avoid confusion, and for clarity, trivial nomenclature has been retained (in this report) for common compounds.

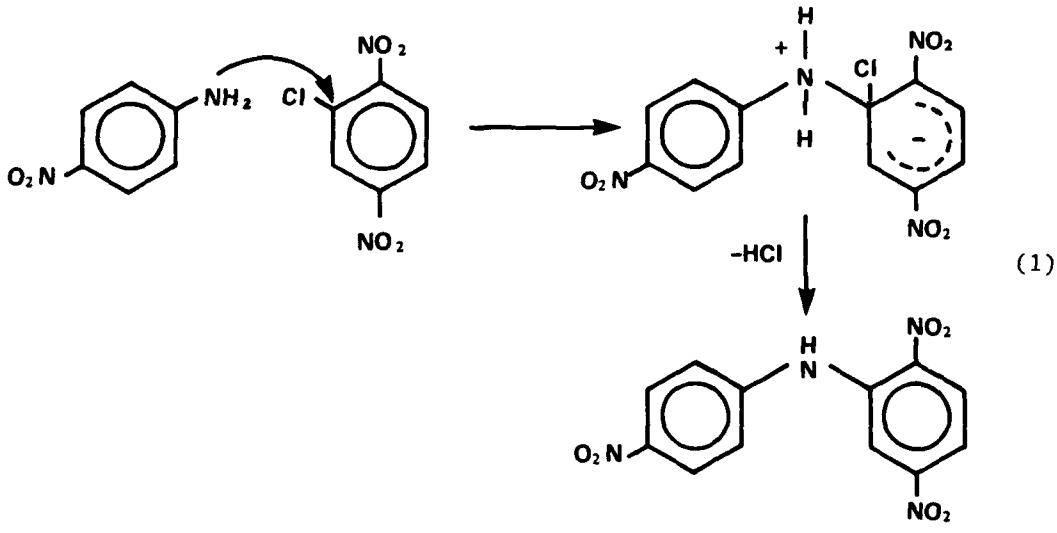
2.1 Condensation methods

The condensation routes are exemplified by the reaction depicted in equation (1) for the preparation of 2,2',4-trinitrodiphenylamine from 4-nitroaniline and 2,4-dinitrochlorobenzene.

This type of reaction has been well studied, particularly for amine nucleophiles, and reviewed(ref.3). Some pertinent observations on the reaction are abstracted below.

The mechanism of the aromatic SN2 reaction is different from the aliphatic case in that a discrete intermediate is formed. This charge-separated Meisenheimer complex subsequently decomposes with elimination of HCl, which is usually effected by the addition of base.

The reaction is greatly enhanced by the presence of electron-withdrawing groups (in this case, nitro), particularly in the 2(6) and 4 positions. Picryl chloride is considerably more reactive (ie shorter reaction times or lower reaction temperature) than 2,4-dinitrochlorobenzene illustrating the cumulative property of the effect. Less reactive are 2- and 4- nitrochlorobenzene. The presence of a nitro group in the 3 position, whilst enhancing the rate relative to the unsubstituted case, is not as activating as the same group in the 2- or 4- positions. Reactivity with amines is not diminished for the 2-halonitrobenzenes compared to the



(1)

4- isomer, and generally the former is more labile, probably due to an internal hydrogen bond stabilising the intermediate. This counteracts any inhibitory effect caused by out of plane distortion which reduces the mesomeric influence. Temporary activation of an aromatic substrate by carboxylic acid has been reported by Ullmann(ref.4). For example, condensation of 3-nitroaniline with 2-chlorobenzoic acid gives 2-(3'-nitrobenzeneamine)- benzoic acid which yields 3-nitrodiphenylamine on decarboxylation.

The nature of the nucleofuge is important and very large differences in rate are encountered. In general, fluoride and nitro are better leaving groups than chloride, bromide and iodide. Activation enthalpies for the reaction of aromatic fluorides with amines are always somewhat lower than for the corresponding chlorides(ref.5). Thus the rate ratio (k_F/k_{Cl}) becomes progressively larger with increasing temperature.

The third important question is the choice of solvent. Because of the production of charge separation in the intermediate, a solvent with high polarity should be used. It is generally found that reactions in dimethylsulphoxide and dimethylformamide proceed at a faster rate than the equivalent processes in benzene and ethanol.

An early paper by Goldberg(ref.6) on the preparation of *mononitrodiphenylamines*, has been influential in later syntheses via the condensation method. The process involved refluxing in nitrobenzene (210°) or bromobenzene (160°) when used as a reactant, in the presence of catalytic amounts of copper or copper(I) iodide. Potassium carbonate was used as a base. This procedure has been reproduced many times since then, with various nucleophiles and electrophilic substrates (vide infra). With the possible exception of the little activated 3- isomer, a copper catalyst

is not required for the reaction to proceed at a reasonably rate (vide infra). This is more so for reaction with the activated dinitro-containing substrates and it has long been known that reactions with picryl chloride require no catalyst(ref.7).

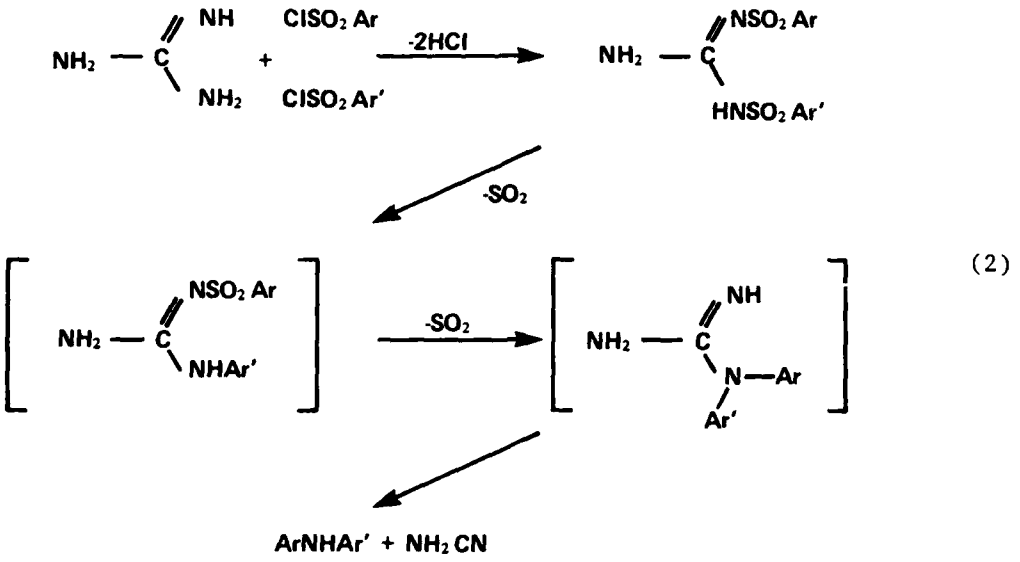
Potassium fluoride(ref.8) has been reported to be useful as a base for condensations with chlorodinitrobenzene. It is unlikely that fluoride substitutes for chloride to form a more reactive substrate(ref.9), given the time-scale of the reaction. These reactions were carried out in the absence of copper or copper(I) iodide. This method has been further extended for the preparations of other nitrodiphenylamines(ref.10), however a report from this laboratory suggests that the yields from this procedure are low(ref.11). In this latter case, however, the lack of agitation of the reaction mixture may have been detrimental. A similar general method has been published using alkali metal hydroxides as bases, the order of effectiveness K>Na>Li indicating some form of catalysis(ref.12). In a recent publication(ref.13) it has been shown that caesium and potassium carbonate are more effective than sodium and lithium carbonate in assisting displacement of the nitro group in DMF or DMSO. A further method has been reported in the patent literature and involves the use of a caustic soda-alumina column(ref.14).

2.2 Degradation of guanidines

A route which involves the decomposition of appropriately substituted guanidines has been developed. The presumed pathway is shown in equation (2).

This procedure has been used successfully for a wide range of mono- and dinitro-diphenylamines, often in essentially quantitative yields(ref.15,16). Degradation of the substituted guanidines is very rapid in boiling aqueous sodium hydroxide and the reaction is complete in one or two minutes. However, the initial formation of the substituted guanidine is not so trivial. This reaction, using the appropriate arylsulphonyl chloride is complicated by the fact that both mono and disubstituted products are obtained, though these may be separated readily(ref.17). Unsymmetric, disubstituted guanidines may be prepared because of this factor(ref.18).

This approach has not been applied to the preparation of tri substituted and higher nitrodiphenylamines and may require some effort to determine correct reaction procedures.



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2.3 Rearrangement and nitration

The final two methods are addressed together since they have the same general problems associated with them. Except in special cases, such methods do not give high yields of single compounds but rather an isomeric mixture. However, when the reaction is stereoselective or if a particular isomer is readily separated then such procedures may be useful. Moreover, the purpose of this report is to detail methods by which samples of reasonably purity may be obtained and thus some of these methods will be discussed. An appreciation of this chemistry is also important in understanding the possible reaction mechanisms which may be operative in the formation of nitrodiphenylamines in propellants.

N-Nitroso derivatives of unsubstituted, mono and dinitrodiphenylamines are known and provide a useful starting material for some isomerisation chemistry.

The Fischer-Hepp rearrangement(ref.19) of N-nitroso aromatic amines in the presence of HCl and HBr may be used to prepare C-nitroso isomerides. The reaction usually proceeds to give mostly the *para* isomer. Subsequent oxidation yields the corresponding nitro compounds. Heating diarylnitrosamines in solvent in the presence of air leads directly to the rearranged C-nitro isomers(ref.20 to 22). A paper has been published dealing with some mechanistic problems associated with this process(ref.20). Aromatic N-nitroamines also rearrange under acid conditions giving directly the C-nitro aromatic amines(ref.20,23). This rearrangement favours the formation of *ortho* products.

Nitration of diphenylamine and its nitro derivatives is often carried out with protection of the aniline nitrogen by nitrosation or acetylation. This is not essential in all cases and nitrations have been performed on

the free base(ref.21). As mentioned before, isomeric mixtures are a problem, though procedures have been developed for the preparations of 2,4'-(ref.24); 4,4'-(ref.24 to 26); 2,2',4- and 2,4,4'-(ref.21) and 2,2',4,4'- isomers(ref.21,26 to 28). Forcing conditions lead to the symmetric hexanitrodiphenylamine(ref.27,29).

3. SYNTHETIC METHODS AVAILABLE FOR SPECIFIC COMPOUNDS

3.1 Mononitro derivatives

All four of the possible C- and N- nitrodiphenylamines have been described. The 2-, 3- and 4- isomers were first prepared by Goldberg(ref.6) via condensation of the relevant nitroaniline (2- and 4- isomers) with bromobenzene (solvent) or nitroacetanilide (3- isomer) with bromobenzene in refluxing nitrobenzene. Catalytic copper with a trace of potassium iodide or copper iodide were used. Both 2- and 4- nitrodiphenylamine are commercially available, though the latter is by far the more expensive. It is useful to note that an alternative entry into the 4- nitro series may be effected via nitration (acetic acid - nitric acid) of diphenylnitrosamine(ref.20). This method gave an approximate 3:1 ratio of the 4- to 2- isomers, which were easily separated via fractional crystallisation.

The thermally unstable N-isomer has been prepared in low yield via reaction of lithium diphenylamide with 2-methylbutyl nitrate(ref.20).

3.2 Dinitro derivatives

The preparations of the following compounds are considered: 2,2'-; 2,4-; 2,4'-; 2,6- and 4,4'-dinitrodiphenylamine.

Both the 2,4- and 2,6- isomers are straightforward to prepare. The former was prepared simply by condensation of aniline with 2,4-dinitrochlorobenzene(ref.24,28,30,31) or 1,2,4-trinitrobenzene(ref.32). Whilst the latter was sythesised from 2,6-dinitrochlorobenzene(ref.33) or the analogous methoxy(ref.34) or nitro(ref.33) compounds. Excess aniline or sodium acetate have been used as the base in these reactions. In addition, the 2,4 isomer is commercially available.

Condensation routes, to the other dinitrodiphenylamines involve coupling of two fragments, each containing one nitro group. This procedure requires more extreme reaction conditions than for the previous examples. Firstly nitroanilines are poorer nucleophiles than aniline itself and secondly the electrophile is only activated by one and not two electron withdrawing groups. Consequently, whereas a short reaction time in refluxing ethanol is sufficient for the preparation of the 2,4- and 2,6- isomers, the other derivatives require much more extreme conditions.

The condensation routes may suffer from oversubstitution giving trinitrotriphenylamines if unprotected anilines are used. N-acetyl protected nitroanilines have been condensed with the appropriate bromobenzenes in nitrobenzene, which after deblocking in refluxing 5:1 ethanol/concentrated HCl gave 67, 42 and 40% yields of the 2,2'-, 2,4'- and 4,4'- isomers, respectively(ref.35). The latter two have been reported, prepared in a similar way, in another source(ref.24). The following is a listing of successful condensation methods using unprotected anilines. The 2,2'- isomer has been made from 2-nitroaniline and 2-bromonitrobenzene(ref.36); the 2,4'- from 4-nitroaniline and 2-nitrobromobenzene in nitrobenzene(ref.24,37); and the 4,4'- isomer from 4-nitroaniline and 4-bromonitrobenzene in nitrobenzene(ref.24,38).

The hydrolyses of substituted guanidines(ref.15) gave 41, 98 and 98% respectively of the 2,2'-; 2,4'- and 4,4'- isomers. In a similar reaction the last isomer was obtained from N,N-bis-(4-nitrophenyl)urea(ref.39).

Nitration of N-acetyldiphenylamine has been used to prepare the 2,4'-(ref.24) and 4,4'-(ref.24 to 26) isomers. An analogous procedure involves the use of the benzoyl moiety as a protecting group(ref.40). Juillard(ref.21) showed that 2,2'and 2,4' dinitrodiphenylamine can be isolated from the reaction mixture by heating 2-nitrodiphenylnitrosamine in 4:1 acetic acid/water. This paper also discussed the relative solubilities of these and the 4,4'- isomer and illustrates how they may be readily separated.

3.3 Trinitro derivatives

The compounds addressed in this report are the 2,2',4-; 2,2',6-; 2,4,4'-; 2,4,6- and 2,4',6- trinitrodiphenylamine isomers.

The 2,4,6- isomer is readily prepared by reaction of aniline with an appropriate picryl derivative, as noted initially by Clemm(ref.24). Apart from the chloride(ref.24): bromide(ref.41), nitro(ref.42), methoxy(ref.43) and nitromethylamide(ref.44) nucleofuges have been used.

Condensation routes have been used successfully for most of the other compounds. The preferred method is the reaction of nitroaniline with a dinitrohalobenzene. For example, the 2,2',4- isomer has been prepared from 2-nitroaniline and 2,4-dinitrobromobenzene in ethanol at 175°(ref.21) or pyridine on a steam bath(ref.45). Carbitol was found to be a superior solvent to nitrobenzene for a preparation of the 2,2'4- isomer analogous to the method of Goldberg(ref.1). The 2,2',6- isomer has been synthesised, in 44% yield, from 2,6- dinitroaniline and 2-nitroiodobenzene(ref.46). The 2,4,4'- derivative was first reported in 1874 and was prepared from 2,4-dinitrobromobenzene and 4-nitroaniline in ethanol at 100°(ref.47). Other authors have described similar methods using the equivalent chloro compound in ethanol(ref.48) and nitrobenzene(ref.24). The preparation of the remaining isomer, substituted in the 2,4',6- positions has not been described though there is no obvious reason why it cannot be prepared by this route.

Nitration and rearrangement routes (via N-nitroso compounds) have been described(ref.21,22) but in general the products are mostly a mixture of the 2,2',4- and 2,4,4'- isomers whose separation by fractional crystallisation is tedious.

3.4 Tetranitro derivatives

The preparations of the 2,2',4,4'-; 2,2',4,6-; 2,2',4',6-; 2,4,4',6- and 2,2',6,6'- isomers are discussed.

The preparations of the picryl derivatives (2,2',4,6- and 2,4,4',6- isomers) are seemingly straightforward although a puzzlingly low yield of the former has been reported. Wedekind(ref.49) prepared these from the nitroaniline and picryl chloride in ethanol solution in 5 and 80% yields respectively. Excess aniline is sufficient to act as the base and a high yield for the 2,3',4,6- isomer (91%) was also obtained. Juillard repeated this procedure(ref.21) without comment on the yield but the low melting point of the product indicated impurity. The 2,4,4',6- isomer was first

reported in 1874(ref.47), prepared by a similar method. Nitration (in acetic acid) of the 2,4,6- trinitro derivative gave a mixture of the 2,2',4,6- and 2,4,4',6- isomers(ref.21) which were separated by fractional crystallisation. The melting point of the 2,2',4,6- isomer obtained in this way was significantly higher than that prepared by the condensation route.

Condensation methods have been reported for the remaining isomers, via reaction of a dinitroaniline with a dinitrohalobenzene. The 2,2',4,4'- isomer has been prepared in poor yield from 2,4-dinitrobromobenzene and 2,4-dinitroaniline by the method of Goldberg(ref.50) and in near quantitative yield in the condensation in the presence of fluoride(ref.8). The latter method has also been reported to be useful for the preparation of the picryl derivatives as well as the 2,2',4',6- isomer, though experimental details and yields were not stated(ref.10).

Nitration routes have been used to prepare the 2,2',4,4' isomer. This may be achieved via N-acetyl diphenylamine(ref.51), diphenylnitrosamine(ref.27) or by direct nitration of unprotected dinitrodiphenylamines(ref.21, 24,28,29). The presence of other isomers has been reported(ref.21) though the major product is the 2,2',4,4' isomer.

4. METHODS USED TO PREPARE AUTHENTIC SAMPLES

4.1 General

The condensation method is obviously general and this approach was taken in the present work. All of the described compounds have been successfully prepared in reasonable yields via the general procedure of reaction of the appropriate aniline with a nitrosubstituted chloro- or fluorobenzene. In preference to nitrobenzene as reaction solvent for the less labile reactions, N,N-dimethylformamide (DMF) or dimethylsulphoxide (DMSO) were used. The advantage of these as solvents is that the work-up procedure is far simpler since addition of the reaction mixture to aqueous acid precipitates the crude product. Nitrobenzene is immiscible with water and must be removed by steam or vacuum distillation. In general, a 100% excess of aniline was used; unreacted starting material was retained in the aqueous acid layer (mononitro anilines) on quenching or extracted by solvent from the crude product. Potassium carbonate, in equimolar proportion to the electrophile, was used as base. Addition of potassium carbonate to the hot reaction mixture gave an intense colouration due to the formation of diphenylamide species. It was not found necessary to use any added catalysts.

The reactions were usually followed by gas chromatography and it was found that for a given class of compound and reaction, differing only in stereochemistry, that the perceived loss of starting materials proceeded at a roughly constant rate. All isolated materials were recrystallised and satisfactory melting points (where literature values were available) were obtained. Purity was also ascertained by thin-layer chromatography. Rf values are given for chromatography on silica using toluene as solvent. Eastman "Chromagram" sheets, no 13181, were used for these measurements, and baked at 100° for 15 min, prior to use. Satisfactory elemental analyses (C, H and N) were obtained for the new compounds (2,4',6-trinitro and 2,2',6,6'-tetranitrodiphenylamine).

4.2 2-, 3- and 4- mononitrodiphenylamine

Both the 2- and 4- isomers are commercially available. The following method, due to Goldberg(ref.6) gave the 3- isomer.

A well agitated mixture of 3-nitroacetanilide (12.0 g, 0.067 mol), bromobenzene (21.0 g, 0.134 mol), potassium carbonate (5.0 g, 0.036 mol), 0.2 g copper powder and 0.2 g copper (I) iodide in 100 mL nitrobenzene was heated at 180° for 16 h and then refluxed (210°) for a further 8 h. Nitrobenzene was removed by steam distillation and the oily residue was added to 100 mL ethanol and filtered. The filtrate was added to 25 mL concentrated HCl and refluxed for 3 h to deprotect the amine and the crude product precipitated by the slow addition of 500 mL water. Two recrystallisations from a minimum volume of boiling 50% aqueous ethanol gave the product as orange flakes. Yield: 7.1 g (50%) mp 108-10°. A sample further purified by column chromatography (silica gel) and recrystallised as above had mp 111-2° lit 112°(ref.50).

4.3 2,4- and 2,6- dinitrodiphenylamine

The 2,4- isomer is commercially available or may be prepared as follows.

Aniline (1.82 mL, 0.02 mol) and 2,4-dinitrochlorobenzene (2.03 g, 0.01 mol) were heated to reflux in 20 mL ethanol, potassium carbonate (1.38 g, 0.01 mol) added and heating continued for a further hour. The product precipitated rapidly on cooling and the reaction mixture was added to 500 mL rapidly stirred 1M HCl. The crude produce was filtered off and recrystallised from 40 mL boiling ethanol, adding enough acetone (ca. 20 mL) to effect dissolution. Yield of orange needles : 1.82 g (70%) mp 157-7.5° lit 157°(ref.52).

The 2,6 isomer was prepared in a similar manner and recrystallised as flat red needles from ethanol. Yield: 1.68 g (65%) mp 106-6.5° lit 107-8°(ref.33).

4.4 2,2'-; 2,4'- and 4,4'-dinitrodiphenylamine

Several methods were attempted using nitroanilines and halonitrobenzenes. Reaction of 2-nitroaniline with 2-fluoronitrobenzene in refluxing DMF gave an excellent yield of the 2,2'- isomer. This procedure was unsatisfactory for the 4,4'- isomer and gave mostly a yellow, acetone-insoluble compound which is probably 4,4',4''-trinitrotriphenylamine. The 2,4'- preparation was apparently also contaminated with an appreciable amount of the triphenylamine. The insolubility of the 2,2'- isomer in DMF probably assists in stopping the reaction at this stage.

Secondly, the reactions were tried using the analogous chloronitrobenzene in DMF, a process which took an appreciably longer reaction time. This proved satisfactory for the 2,2'- isomer and also a moderate yield of the 4,4'- isomer was obtained. The latter still contained some less soluble material which had to be removed.

Finally, the reaction with the chloronitrobenzene in refluxing DMSO was found to be useful for the preparations of the 2,4'- and 4,4'- isomers though the latter was still contaminated with insoluble material.

The 2,2'- isomer was prepared as follows. 2-Nitroaniline (3.04 g, 0.022 mol) and 2-fluoronitrobenzene (2.11 mL, 0.02 mol) were heated to reflux in 20 mL DMF and potassium carbonate (2.8 g, 0.02 mol) added. The resultant deep red mixture was refluxed for a further 2 h and then cooled. The reaction mixture, which had solidified to a mass of needles was then washed into 500 mL rapidly stirred 1M HCl with ethanol. The crude product was filtered off and recrystallised from a minimum volume of boiling 1:1 ethanol/acetone (ca. 160 mL). Yield of flat, orange needles : 4.02 g (78%) mp 172.5-3° lit 172-2.5°(ref.1).

The following procedure was also used. 2-Nitroaniline (2.76 g, 0.02 mol) and 2-chloronitrobenzene (1.58 g, 0.01 mol) were heated to reflux in 20 mL DMF, potassium carbonate (1.38 g, 0.01 mol) added and the mixture heated for a further 24 hr. The cooled reaction mixture was washed into 500 mL rapidly stirred 1M HCl, with ethanol, and the product collected by filtration. The crude product was further purified by dissolution in 200 mL dichloromethane and washing with M HCl (3 x 200 mL) and water. The dried and evaporated residue was decolourised with carbon in 100 mL acetone and precipitated by the addition of 400 mL water to the filtrate. Recrystallisation from 35 mL of boiling 1:1 ethanol/acetone gave 1.02 g (39%) of the product mp 171-2°.

The 2,4'- isomer was prepared, in a similar method to that above, from 2-nitroaniline and 4-chloronitrobenzene in DMSO (90 min) reflux. The lower solubility of the 2,4'- isomer required that the decolourising to be carried out in 200 mL acetone and the product reclaimed by the addition of 4 volumes water. Yield of red, fluffy needles after recrystallisation from ca. 60 mL boiling acetic acid : 1.30 g (50%) mp 222-3° lit 224-4.5°(ref.1). A poorer quality product was obtained from the reaction in DMF.

The 4,4'- isomer was prepared analogously using DMSO as reaction solvent. The crude product obtained by quenching the reaction mixture in 1M HCl was dissolved in 400 mL dichloromethan/100 mL ethanol and washed as before. The product was decolourised in 200 mL acetone and recrystallised by boiling the precipitate with 200 mL ethanol, filtering and evaporating the filtrate on a hot-plate until crystallisation started. Yield of red-orange needles 1.36 g (53%) mp 217-8° lit 217.5-8°(ref.1). The same reaction in refluxing DMF gave a 31% yield of the product, which was recrystallised in a similar fashion (mp 217-8°). The colour of the compound is strongly particle size dependent and varies from red to yellow (for fine crystals).

4.5 2,4,6- trinitrodiphenylamine

Picryl chloride (2.48 g, 0.01 mol) was heated to reflux in 30 mL ethanol and aniline (2 mL, 0.022 mol) added. The reaction mixture solidified in less than two minutes, and after heating for a total of 5 min, the cooled mixture was added to 500 mL 1M HCl. The product was crystallised from the minimum volume of boiling ethyl acetate (ca. 30 mL) as large orange needles. Yield 2.49 g (82%) mp 180-1° lit 179.5-80°(ref.24).

4.6 2,2',4-; 2,2',6-; 2,4,4'- and 2,4',6-trinitrodiphenylamine

The preparations of these compounds are similar and exemplified by that for the 2,2',4 isomer.

2-Nitroaniline (2.70 g, 0.02 mol) and 2,4-dinitrochlorobenzene (2.03 g, 0.01 mol) were heated to reflux in 20 mL DMF and potassium carbonate (1.38 g, 0.01 mol) added. An immediate colour change from yellow to intense red was seen and the heating continued for a further hour. The cooled mixture was washed into 500 mL rapidly stirred 1M HCl, with ethanol (20 mL). The yellow precipitate was collected and partitioned between 200 mL dichloromethane and 1M HCl (3 x 200 mL) and the dichloromethane layer washed with water (200 mL). After drying and evaporation, the product was decolourised in 100 mL acetone and precipitated by the addition of one volume of water. This precipitate was filtered off and washed with a few mL ice-cold methanol to remove some highly coloured, brown material. Recrystallisation from a minimum of boiling 1:1 methanol/acetone (ca. 160 mL) gave 1.51 g (50%) of lustrous yellow plates mp 186-7° lit 187.5-8°(ref.1).

Preparations of the other isomers were achieved in similar fashion, as follows, along with pertinent modifications.

The crude 2,2',6- isomer was partitioned between 400 mL dichloromethane and aqueous acid, and subsequently decolourised in 250 mL acetone. The product was recrystallised from a minimum of boiling 1:1 methanol/acetone (ca. 320 mL) and isolated as yellow needles. Yield 1.72 g (57%) mp 228.5-9° lit 222°(ref.46).

The crude 2,4,4'- isomer was decolourised in 200 mL acetone and later recrystallised from a minimum volume (ca. 90 mL) of boiling 1:1 methanol/acetone to give 1.18 g (39%) of a yellow fibrous crystalline mass mp 188-90° lit 193°(ref.10).

The 2,4',6- isomer was prepared as for the 2,2',4 derivative and recrystallised from 50 mL boiling methanol with the addition of sufficient acetone to effect dissolution (ca. 7 mL). Yield of yellow needles : 1.48 g (49%) mp 160-1°.

4.7 2,2',4,6- and 2,4,4',6 tetranitrodiphenylamine

The latter was easily prepared as follows.

4-Nitroaniline (2.76 g, 0.02 mol) and picryl chloride (2.48 g, 0.01 mol) were heated to reflux in 30 mL ethanol and potassium carbonate (1.38 g, 0.01 mol) added. After 1 h further reflux, the cooled reaction mixture was quenched by addition to 500 mL rapidly stirred 1M HCl. The precipitate obtained was dissolved in 500 mL dichloromethane and washed with 1M HCl (2 x 100 mL) and then water. The dried, evaporated product was recrystallised from a minimum volume of boiling 1:1 ethanol/acetone (ca. 150 mL). Yield of yellow blocks : 1.95 g. The filtrate was evaporated and recrystallised as above to give a further crop of the same material. Total yield 2.26 g (65%) mp 222-3° lit 223°(ref.53).

As discussed before, the condensation route for the preparation of the 2,2',4,6- isomer has been reported to give only a very small yield(ref.49) and this was again encountered. In a similar preparation to that for the 2,4,4',6- isomer but with the modification that the aniline and potassium carbonate were heated to reflux before addition of picryl chloride, and the reaction mixture heated for a further 4 h; a 12% yield was obtained. The yellow crystalline material had mp 238-9° lit 234°(ref.21) after recrystallisation from 1:1 ethanol/ethyl acetate (ca. 130 mL).

Alternatively, the product was obtained from the reaction of 2,4,6-trinitroaniline (2.28 g, 0.01 mol) with 2-fluoronitrobenzene (1.17 mL, 0.011 mol) in 20 mL DMF. Following addition of potassium carbonate (1.38 g, 0.01 mol) the mixture was heated for a further hour, cooled and added to 500 mL rapidly stirred 1M HCl. The resultant precipitate was collected and washed on the filter with hot 1M HCl. The brown precipitate was decolourised in acetone (200 mL) and recovered by the slow addition of 400 mL water. This decolourisation procedure was repeated to yield a yellow precipitate which was recrystallised from ca. 130 mL boiling 1:1 ethanol/ethyl acetate. Yield of yellow needles : 0.55 g (16%), mp 239-40°. TLC analysis (toluene/silica) of this compound showed an identical Rf to that prepared from picryl chloride and a mixed melting point with this exhibited no depression. This preparation confirms the structure of the product. Elemental analysis (CHN) was also consistent with a tetranitrodiphenylamine.

4.8 2,2',4,4'-; 2,2',4',6- and 2,2',6,6'- tetranitrodiphenylamine

These are all readily prepared from the appropriate dinitroaniline and dinitrochlorobenzenes as is illustrated for the 2,2',4,4' isomer.

2,4-Dinitrochlorobenzene (2.03 g, 0.01 mol) and 2,4-dinitroaniline (3.76 g, 0.02 mol) were heated to reflux in 20 mL DMF and potassium carbonate (1.38, 0.01 mol) added. The deep red mixture was left to reflux for a further 30 min, cooled and washed into 500 mL rapidly stirring 1M HCl. The crude product was filtered and the precipitate washed with portions (5 x 100 mL) of hot (80°) 1M HCl to remove excess aniline. The precipitate was then decolourised in 100 mL acetone and recovered by the addition of 200 mL water. Recrystallisation was from the minimum volume of boiling 1:1 ethanol/acetone (ca. 250 mL). Yield of yellow blocks : 1.70 g a second crop of the same material was obtained by evaporation of the filtrate and recrystallisation from the same solvent. Total yield: 2.22 g (64%) mp 202-3° lit 203.5-4°(ref.1).

The 2,2',4',6- isomer was made similarly, from 2,4-dinitroaniline and 2,6-dinitrochlorobenzene, and recrystallised from ca. 100 mL boiling 1:1 ethanol/acetone. Yield of long yellow needles : 2.85 g (82%) mp 182-3°. The melting point obtained is significantly lower than the single report in the literature: 196-7°(ref.10). Thin layer chromatography indicates that the recrystallised product is not unreacted 2,4-dinitroaniline (mp 176-8°) and elemental analysis (CHN) was consistent with the formulation as a tetranitrodiphenylamine.

The 2,2',6,6' isomer was prepared in analogous manner except that excess aniline was extracted from the initial product by ether (200 mL) rather than hot HCl which proved ineffective. The product was decolourised as before and recrystallised from a minimum of boiling 1:1 ethanol/ethyl acetate (ca. 100 mL). Yield of yellow blocks 0.98 g (28%) mp 234-5°.

5. RESULTS AND DISCUSSION

The condensation route, reacting appropriately substituted anilines with halonitrobenzene appears to be the most general and easily adapted method available. Other methods are however suitable for specific compounds and in some cases give a superior yield.

All of the title compounds have been prepared by this route from cheap and readily available starting materials. With the exception of two compounds, the yields range from moderate to excellent. A lower yield was obtained for the 2,2',6,6'- derivative which may be a result of excessive steric hindrance. The 2,2',4,6- derivative is difficult to obtain by this method, as noted previously, though it may be prepared in a low yield.

Thus a general method to those nitro derivatives, likely to be formed in propellants when diphenylamine and related compounds are used as stabilisers, is established and is summarised in Table 1.

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TABLE 1. SYNTHESIS AND PHYSICAL DATA FOR THE COMPOUNDS STUDIED

Isomer	Reagents	Reaction solvent	Reaction time	Melting point (°)	Recrystallisation solvent	Yield (%)	Rf (Toluene/SiO2)
Unsubstituted	Commercial sample						0.89
2	Commercial sample						0.87
3	3-Nitroacetanilide Bromobenzene	Nitrobenzene	24h	112 lit 112(ref.50)	ethanol-water	50	0.75
4	Commercial sample						0.51
2,4	Aniline 2,4-Dinitrochlorobenzene	Ethanol	1h	157-7.5 lit 157(ref.52)	ethanol-acetone	70	0.76
2,6	Aniline 2,6-Dinitrochlorobenzene	Ethanol	1h	106-6.5 lit 107-8(ref.33)	ethanol	65	0.79
2,2'	2-Nitroaniline 2-Fluoronitrobenzene	DMF	2h	172 .5-3 lit 172-2.5 (ref.1)	ethanol-acetone	78	0.72
	2-Nitroaniline 2-Chloronitrobenzene	DMF	24h	171-2	ethanol-acetone	39	
2,4'	2-Nitroaniline 4-Chloronitrobenzene	DMSO	1.5h	222 -3 lit 224-4.5 (ref.1)	acetic acid	50	0.69
4,4'	4-Nitroaniline 4-Chloronitrobenzene	DMSO	1.5h	217 -8 217.5-8(ref.1)	ethanol	53	0.11
	4-Nitroaniline 4-Chloronitrobenzene	DMF	24h	217-8	ethanol	31	
2,4,6	Aniline Picryl chloride	Ethanol	5 min	180-1 lit 179.5-80 (ref.24)	ethyl acetate	82	0.76

TABLE 1(CONTD.).

Isomer	Reagents	Reaction solvent	Reaction time	Melting point (°)	Recrystallisation solvent	Yield (%)	Rf (Toluene/SiO2)
2,2',4	2-Nitroaniline 2,4-Dinitrochlorobenzene	DMF	1h	186-7 lit 187.5-8 (ref.1)	methanol-acetone	50	0.54
2,2',6	2-Nitroaniline 2,6-Dinitrochlorobenzene	DMF	1h	228.5-9 lit 222(ref.47)	methanol-acetone	57	0.62
2,4',4	4-Nitroaniline 2,4-Dinitrochlorobenzene	DMF	1h	188-90 lit 193(ref.10)	methanol-acetone	39	0.42
2,4',6	4-Nitroaniline 2,6-Dinitrochlorobenzene	DMF	1h	160 -1	methanol-acetone	49	0.46
2,2',4,6	2-Nitroaniline Picryl chloride	Ethanol	4h	239 -40 lit 235(ref.21)	ethanol-ethyl acetate	12	0.61
	2,4,6-Trinitroaniline 2-Fluoronitrobenzene	DMF	1h	239-40	ethanol-ethyl acetate	16	
2,4,4',6	4-Nitroaniline Picryl chloride	Ethanol	1h	222-3 lit 223(ref.53)	ethanol-acetone	65	0.34
2,2',4,4'	2,4-Dinitroaniline 2,4-Dinitrochlorobenzene	DMF	30 min	202-3 lit 203.5-4 (ref.1)	ethanol-acetone	64	0.30
2,2',4',6	2,4-Dinitroaniline 2,6-Dinitrochlorobenzen	DMF	30 min	182-3 lit 196-7 (ref.10)	ethanol-acetone	82	0.40
2,2',6,6'	2,6-Dinitroaniline 2,6-Dinitrochlorobenzene	DMF	30 min	234-5	ethanol-ethyl acetate	28	0.72

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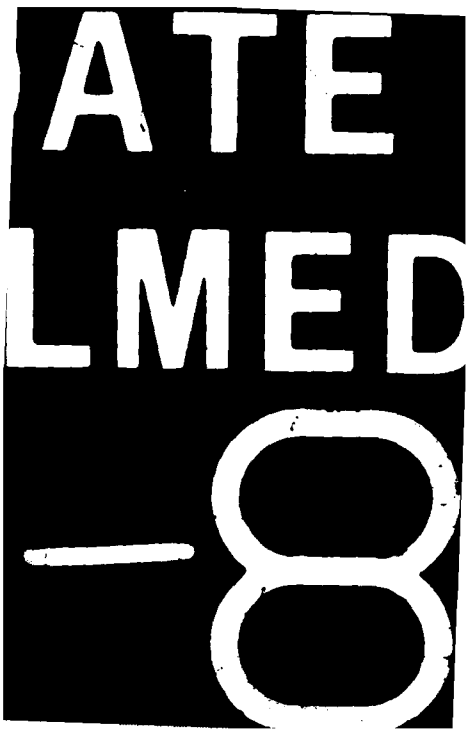
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